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Development of internal structure of polymer-modified asphalts via transformations of the reduced frequency

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Abstract

The independent variable of dynamic material functions and corresponding master curves, the reduced angular frequency $\overline{\omega}$, was transformed into the apparent molecular weight MW*. As a function of MW*, the normalized master phase angle represented an apparent cumulative molecular weight. This function's numerical differentiation yielded the probability density function of the apparent molecular weight, f(MW*). While this procedure is unproblematic in conventional (straight run) asphalts, it is yielding peaks of negative MW* in polymer modified asphalts. Thus reduced frequency was also transformed to the temperature, which allowed us to determine that the apparent glass transition temperature as the maximum on the master curve of loss modulus G″(T). The master curve of the normalized phase angle as a function of temperature helped to explain the phenomenon associated with the probability density function in modified asphalts. The results presented in this article were obtained numerically, without the use of rheological models.

KEYWORDS

colloids, copolymers, rheology, structure-property relationships

1 | INTRODUCTION

Asphalt, one of the oldest engineering materials, is chiefly used for construction of pavements,[1,2] but other technologies can also make use of this material.[3] This contribution defines asphalt as any "dark brown to black cementitious material in which the predominant constituents are bitumens which occur in nature or are obtained in the petroleum processing."[4] As in many other materials, the linear response function of asphalt gives the theoretical (phenomenological) basis for the study of properties of asphalt.[5,6] In linear viscoelasticity, the generalized response function is represented by the complex modulus G*(ω), which is a complex function of the angular frequency ω.[5,6] The complex modulus is commonly determined by dynamic experiments where the small periodic shear strain acts as an input and the resulting

out-of-phase shear stress is the output. Both shear strain and shear stress are periodic, with the same frequency ω.

Various models of G*(ω) have been used in studies of the linear viscoelastic behavior of complex viscoelastic materials.[7,8] Such materials have a "memory" in that they can "remember" deformations occurring from time $-\infty$ up to the present observation time, t. Since $\omega \sim 1/t$, G*(ω) should be known on interval frequencies that are as wide as possible. Fortunately, this is not a grave constraint because many materials belong to the set of rheologically simple materials[3,7,9] in which time–temperature superposition (tTs) can be used.[7,8] The complex modulus, G*(ω), is given in two forms[10]:

$$\text{Polar form} : G * (\omega) = |G * (\omega)| \exp[i\delta(\omega)], i = \sqrt{-1}, \quad (1)$$

where δ(ω) represents the phase shift between the shear stress and the shear strain, or

$$\text{Cartesian form}: G^*(\omega) = G'(\omega) + iG''(\omega), \qquad (2)$$

where the storage modulus $G'(\omega)$ is related to the average energy stored and released per cycle and the loss modulus $G''(\omega)$ is related to dissipation in a complete cycle.

The tTs principle leads to the following reduced dynamic quantities[7,11,12]: the reduced frequency, $\bar{\omega} = a_T \omega$; the reduced storage modulus $G'(\bar{\omega})$; the reduced loss modulus $G''(\bar{\omega})$; and the reduced loss tangent $\tan(\delta(\bar{\omega})) = G''(\bar{\omega})/ G'(\bar{\omega})$. The horizontal shifting factor in asphalt materials a_T is well described by the Williams-Landel-Ferry (WLF) equation as,[7]

$$\log a_T(T; T_r) = [-C_1(T - T_r)]/[C_2 + (T - T_r)], \qquad (3)$$

where T is the test temperature, T_r is the reference temperature and C_1, C_2 are parameters of the WLF model.[3,7,8]

In many polymeric materials, the vertical shifting factor is close to 1. In asphalts, however, vertical shifting is required to obtain smooth and continuous master curves for the dynamic functions. The commercial software IRIS[11] was used to obtain the reduced dynamic master curves in most of the materials discussed in this contribution.

1.1 | Transformation of the reduced frequency axis to an apparent molecular weight in asphalt

In the later part of the 20th century, the Bituminous Materials Chair worked on the rheological characterization of conventional as well as polymer modified asphalt binders. This work was based on the linear viscoelastic models of the relaxation modulus, G(t), see, for example.[6,10,13] The work of Tuminello,[14] and Wu,[15] on the possibility to obtain the MWD of polymers from the rheological data was known to the Chair and thus an attempt to use this method for asphalt binders was persuaded.

More recently, Cuciniello et al.[9,27] compared the phase angle method discussed by Tuminello,[14] to the GPC results for conventional asphalts. In these cases, master curves of phase angle were constructed and then used to calculate the molecular weight distribution (MWD). One of the crucial elements in this procedure is the calibration equation. This equation relates the molecular weight of asphalt to the reduced angular frequency, $\bar{\omega}$, which is the independent variable of the dynamic master curves.[6,9,13,16]

As in polymers[14,15,17,18] the model of G(t) was crucial to such attempts. Calculation of MWD was promising in conventional asphalt binders; however, in polymer modified asphalt binders an unphysical (negative) peaks on MWD were obtained (8.9) and the research work in this direction was abandoned by the Chair. Themeli et al.[19] resurrected the work of the Chair and obtained MWDs of several asphalt binders; however, none of them polymer modified.

After almost two decades, we decided to prepare a "final" manuscript dealing with the MWD of asphalt materials. At first it was realized, that the term "MWD" should be changed to an "apparent MWD" and that the model of the relaxation modulus is not needed. Thus, the dynamic experimental data of the normalized phase angle for the construction of the apparent MWD in asphalt materials accompanied by numerical methods for smoothing and differentiation were used. It is probably more realistic to assume that from rheology one has a chance to determine only an apparent molecular weight. Such a quantity can give an approximate picture of the internal composition of asphalt materials; both, conventional as well as polymer modified. The distribution of sizes/weights of various parts of the whole material can be approximated. Because of possible interactions between many parts of the studied material some peaks of such apparent MWD can be identified as virtual parts of the whole sample. By this way, at least the largest/strongest, elements/agglomerations in the studied material can be estimated.

In what follows, the master curves of dynamic material functions of the studied materials were used. No model fitting of the storage, loss moduli, or phase angle was performed in order to obtain relaxation or retardation spectra. Shifted dynamic experimental data were visually cleaned and continuous master curves were used for further analysis.

The reduced frequency was transformed into the molecular weight via the power law relation

$$M = K(\bar{\omega})^{-\alpha}, \qquad (4)$$

where M represents the molecular weight and K and α are model parameters.[6,9,10,16]

There is a variety of different methods to determine molecular weight, any of which can be used in Equation (4). For example, Zanzotto et al.[16] use a molecular weight obtained by vapor pressure osmometry. Of course, the calibration equation depends on the type of molecular weight that was used. In this article, we follow the procedure suggested by Themeli et al.[19] and use MW* for the molecular weight without specifying the method by which MW* was determined. From the normalized phase angle $2\delta(\bar{\omega})/\pi$ and the calibration Equation (4), the cumulative molecular weight can then be defined as:

$$2\delta(\bar{\omega})/\pi = \text{cum f(MW}*), \qquad (5)$$

where the function f(MW*) is classically the probability density function of molecular weight MW*. If F(MW*) is the distribution function, then Themeli et al.[19] give us the following:

$$F(a \leq \log MW* \leq b) = \int_a^b f(MW^*) d\log MW^*, \qquad (6)$$

and

$$\text{cum f(MW}^*) = \int_0^{\log M^*} f(MW^*) d\log MW^*, \qquad (7)$$

with the normalization condition

$$\int_0^\infty f(MW^*) d\log MW^* = 1. \qquad (8)$$

The probability density f(MW*) is then

$$f(MW*) = {d\,\text{cum}(f(MW^*))}\big/{d\log MW^*}. \qquad (9)$$

From the assumptions in Equation (5), it follows that the function f(MW*) can be obtained by differentiating the master curve of the normalized phase angle. Time–temperature shifting was used in most cases, and the dynamic master curves were produced with the help of the IRIS software package.[11] From the dynamic master curves, we obtained the normalized phase angle $2\delta(\varpi)/\pi$.

The derivative of the normalized phase angle, $\frac{d\left[\frac{2\delta(\log MW^*)}{\pi}\right]}{d\log MW^*}$, was calculated numerically with the help of the commercial software package Tablecurve.[20] The data from the normalized phase angle was initially reduced in size with a spline digital filter.[21] This also produced uniformly spaced data to which the Svitzsky-Golay smoothing and noise reduction algorithm was applied.[22] The same algorithm also provided enhanced and smoothed derivatives up to an order of four. By applying this procedure to the phase angle's master curves, the function f(MW*) was obtained for all studied asphalt materials.

Conventional asphalt is chemically complex material[2,3] that exhibits a viscoelastic behavior resembling the behavior observed in low-molecular weight polymers.[7,10] It is common to modify asphalt with a variety of polymers and additives to improve its engineering properties. Such modifications complicate the internal structure of asphalt. From the point of industrial applications, it is beneficial to know how the structure of conventional and modified asphalt responds to various deformations.

In this paper, a concept of the transformation of angular frequency $\bar{\omega}$ (an independent variable of master curves of dynamic material functions) to the apparent molecular weight MW* was investigated in aged conventional asphalt as well as modified asphalts with a variety of modifiers.

2 | MATERIALS AND METHODS

Two conventional asphalts from different sources and distilled to different penetration grades were used in this study. The first conventional asphalt "U" was prepared by vacuum distillation of crude oil to 50/70 penetration. The rolling thin film oven test (RTFOT)[23] and pressure aging vessel (PAV)[23] aged samples were denoted as "R", and "P" The second conventional asphalt, a commercial product of Husky Energy, was prepared by vacuum distillation of crude oil to 200/300 penetration and denoted as "B." Two different modification technologies were used on asphalt B: either by thermoplastic elastomer, styrene-butadiene-styrene (SBS), SBS D1101 from Kraton Performance Polymers, Inc, or by the reactive ethylene terpolymer Elvaloy 4170 from Dow Chemicals. In some cases, SBS-modified asphalt blends were cross-linked by technical sulfur. In several samples the polyphosphoric acid PPA 115 from Innophos Inc. was also used as a modifier/additive. Information about the preparation of the polymer modified asphalt blends from the B samples can be found in Ref. 3.

The characterization of polymer modified asphalt blends from conventional asphalt B according to Superpave binder specification (AASHTO M320)[23] is shown in Table 1. Note, that sample "B-PDS which was asphalt B +3 wt% SBS Kraton D1101 + 0.12 wt% sulfur + 2.2 wt% PPA" represents an extreme case of polymer modified asphalt. The value of viscosity@135°C[23] for this modified asphalt was 7628 mPa.s, thus the determination of minimum service temperature by Bending Beam Rheometer[23] was not possible.

The dynamic material functions of asphalt U were investigated using a DSR-Anton Paar MCR301.[9] Group B of asphalt blends was tested in ARES–G2 rheometer of TA.[3] The master curves of the normalized phase angle (with independent variable log ($\bar{\omega}$) at reference temperature $T_r = 0°C$), were prepared for all cases to which the calibration Equation (4) was applied.

3 | EXPERIMENTS AND THE NUMERICAL RESULTS

The calibration Equation (4) is of obvious and paramount importance for achieving a reasonable estimate of the

TABLE 1 Characterization of polymer modified asphalt blends from conventional asphalt B according to superpave binder specification

Asphalt material	Superpave PG[a]	Continuous PG
B, 200/300 penetration	PG 52–34	PG 52.9–34
B + 3 wt% SBS Kraton D1101	PG 58–31	PG 63.3–33
B + 3 wt% SBS Kraton D1101 + 0.16 wt% S	PG 64–34	PG 67.2–36
B + 1 wt% Elvaloy 4170	PG 58–34	PG 61.9–36
B + 2 wt% Elvaloy 4170	PG 64–34	PG 65.1–35
B + 1.5 wt% Elvaloy 4170 + 0.2 wt% PPA	PG 64–34	PG 68.1–35
B + 1.5 wt% Elvaloy 4170 + 0.6 wt% PPA	PG 76–34	PG 76.1–35
B + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur + 0.2 wt% PPA	PG 70–34	PG 71.6–36
B + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur + 2.2 wt% PPA	PG 88-XX	PG 100-XX

[a]The split grade was reported for minimum service temperature.

FIGURE 1 Asphalt U, 50/70 penetration: ● conventional (unaged), △ R-aged (RTFO), ◇ P-aged (PAV). f(MW*), apparent molecular weight

FIGURE 2 Asphalt B, 200/300 penetration: ● conventional, △ B + 3 wt% SBS Kraton D1101, ◇ B + 3 wt% SBS Kraton D1101 + 0.16 wt% S

MWD. In 1990s, it was shown that the parameters of the calibration equation depend not only on the method used to determine the molecular weight, but also on the type of base asphalt used.[6,13,16] Roughly speaking, $K \sim 3$ and $\alpha \sim 0.1$ for conventional unmodified asphalts can be used. Here, we use the calibration equation given by Themeli et al.,[19]

$$\log(MW*) = 2.88 - 0.06768 \log \bar{\omega}, \quad (10)$$

for master curves constructed at the reference temperature $T_r = 0°C$ and with MW* representing an apparent molecular weight rather the one defined a priori.

Figure 1 shows the probability density f(MW*) for conventional asphalt U and its aged samples R (RTFO) and P (PAV).[3,9] It is encouraging to see that the function f(M*) was able to distinguish between the two artificial aging processes that were applied to conventional asphalt U.

It is known, that when conventional asphalt B with its high-penetration value (low viscosity) was modified by polymers and some additives, the graph of f(MW*) had the potential to contain at least one negative peak.[6,10,13,16] Such peaks are not artifacts that can be eliminated by a "proper" baseline. The negative peaks of f(MW*) were identified by Stastna et al.[10] by the general model of the complex modulus. It has been noted that negative peaks in the derivative of the phase angle can be a part of a
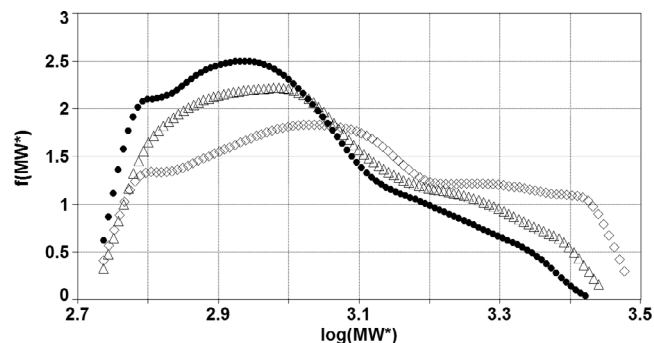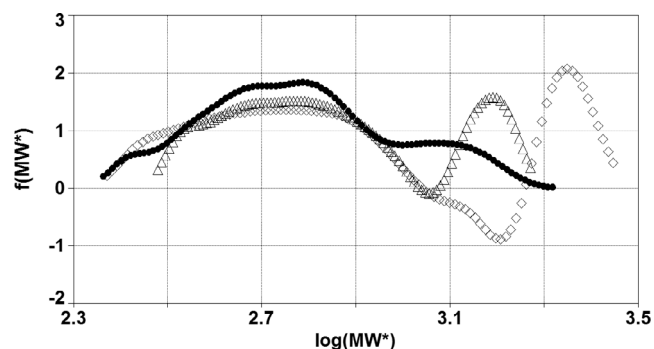
"pseudospectrum" of the polymer modified asphalt blends that are described by a generalized complex modulus in the form of a complex rational function.[6,10] For example, the function f(MW*) in Figure 2 shows conventional asphalt B, which was modified by 3 wt% of SBS Kraton D1101 with and without sulfur as a vulcanizing agent. The first small negative peak was generated by SBS. The large negative peak appeared in the modified asphalt blend with the same amount of SBS and a small amount of sulfur used for cross-linking.

In such cases, it is very difficult to call f(MW*) the probability density. It was suggested that the negative peaks on the function f(MW*) might represent the interphase interactions in modified asphalts.[6,13,16] This is another reason to refer to the derivative of the normalized phase angle that has been transformed to an apparent molecular weight (i.e., f(MW*)) as an apparent MWD.

Similar to the situation with the blends of asphalt B that were modified with SBS Kraton D1101 cross-linked with sulfur, negative peaks are also evident in the blends of asphalt B modified by reactive elastomeric terpolymer Elvaloy 4170. This becomes more evident as the
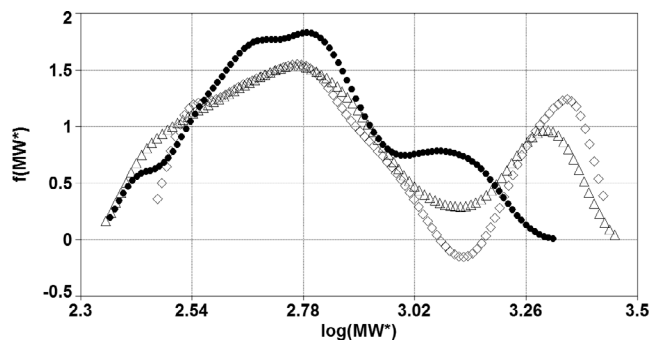
FIGURE 3 Asphalt B, 200/300 penetration: ● conventional, Δ B + 1 wt% Elvaloy 4170, ◇ B + 2 wt% Elvaloy 4170

FIGURE 4 Asphalt B, 200/300 penetration: ● conventional, Δ B + 1.5 wt% Elvaloy 4170 + 0.2 wt% PPA, ◇ B + 1.5 wt% Elvaloy 4170 + 0.6 wt% PPA

FIGURE 5 Asphalt B, 200/300 penetration: ● conventional, Δ B + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur+0.2 wt% PPA, ◇ B + 3 wt% SBS Kraton D1101+ 0.12 wt% sulfur +2.2 wt% PPA

concentration of polymer increases (Figure 3). The negative peaks are more pronounced in the presence of PPA, which, according to manufacturer, works as a catalyst for curing of Elvaloy type terpolymers (Figure 4). The impact of PPA on the blends of asphalt B with SBS Kraton D1101 and a small amount of sulfur is shown in Figure 5. PPA is used in polymer modified asphalt asphalts to lower the amount of polymer modifier.[2,3] Discussion of use of PPA in asphalt can be found in ref. 3 and the references cited therein.

It is now clear that the derivative of the cumulative apparent molecular weight (i.e., f(MW*)) should not be generally considered the same as the classical probability density of the molecular weight of polymer modified asphalts. This does not mean that the information contained in f(MW*) is useless. On the contrary, this function's graphs, which were obtained almost exclusively via numerical methods, can help build an understanding of the structural changes in both modified and unmodified asphalts.

3.1 | Transformation of the reduced frequency axis to the temperature

After the master curves of the dynamic material functions have been obtained, it is easy to transform the reduced frequency $\bar{\omega} = a_T \omega$ to the temperature T. The logarithm of $\bar{\omega}$ is

$\log \bar{\omega} = \log a_T + \log \omega = -C_1(T - T_r)/[C_2 + (T - T_r)] + \log \omega$, where the WLF form of a_T is used. The temperature is then given as

$$T = T_r + \frac{C_2 \log(\omega/\bar{\omega})}{C_1 - \log(\omega/\bar{\omega})]}. \quad (11)$$

It then becomes possible to transform $G'(\bar{\omega})$, $G''(\bar{\omega})$, and tan $\delta(\bar{\omega})$ with the help of Equation (11) to obtain, with a careful problem statement, a different
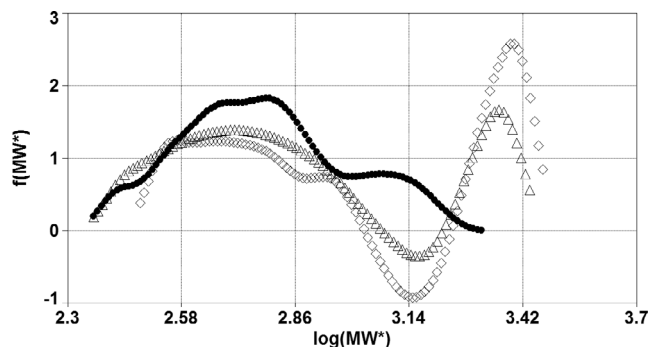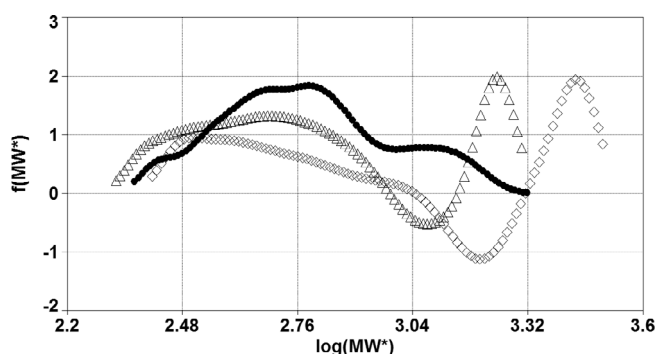
"experiment:" the temperature ramp experiment. In other words, in a thermodynamically homogeneous external system characterized by the reference temperature T_r, the temperature of the tested material sample changes on the interval $(T_{max} \rightarrow T_{min})$. As the temperature changes, the material undergoes a small periodic shear with a constant test frequency ω. Thus, the transformation of the reduced frequency yields a "mirrored" image resembling the temperature ramp experiment with a test frequency of ω and a rate of change of T that is determined by the width of the reduced frequency interval.

Probably the most interesting transformation is that of the loss modulus $G''(\bar{\omega})$, which has a strong absolute maximum at high-reduced frequencies.[3] After the transformation $\bar{\omega} \rightarrow T$, the position of this maximum determines the glass transition temperature interval. The position of the maximum is usually denoted as the tested material's apparent glass transition temperature, T_g. In asphalt where $T_r = 0°C$ and $\bar{\omega} = 10$ rad/s, T_g is about $-22°C$. The question of the appropriate testing frequency is discussed by Seyler.[24] The frequency in temperature
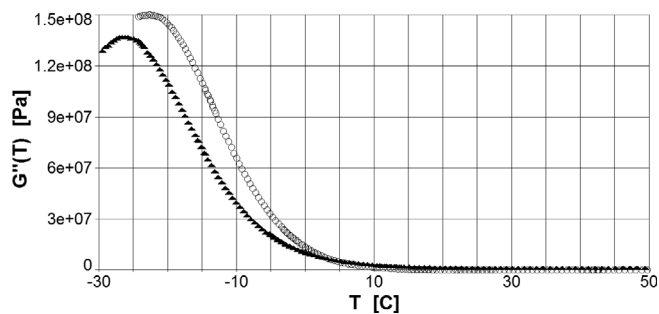
FIGURE 6 Asphalt B, 200/300 penetration, $\bar{\omega} \rightarrow T$: ○ conventional, $T_g \sim -22.7°C$, ▲ B + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur+2.2 wt% PPA, $T_g \sim -26.7°C$

ramp testing should be as small as 0.01 Hz, and the rate of change of temperature should vary from 1 to 20°C per minute. In the method suggested in this note, the estimated rate of change of T is much smaller and must therefore be considered part of the discussion of this experiment.

In practical terms, the starting point was again the dynamic material functions' master curves. The reference temperature for the asphalts was again 0°C. A testing frequency of 10 rad/s was chosen for transformation of $\bar{\omega} \rightarrow$ T. Conventional asphalts and modified asphalts from group B (200/300 penetration) were both investigated. The asphalt U (50/70 penetration) and its aged variations were not tested at low-enough temperatures to show the absolute maximum of $G''(\bar{\omega})$, and are thus excluded from this part of study.

The glass transition temperatures of the tested asphalts, which were determined from the positions of the maxima on the graphs of $G''(T)$, were between −22 and − 24°C for conventional asphalt B when it was modified with SBS Kraton D1101 or Elvaloy 4170 and with the cross-linking/curing additives sulfur and PPA. Figure 6 shows the loss moduli $G''(T)$ of conventional asphalt B and the modified B-PDS, which contains 3 wt% SBS Kraton D1101, 0.12 wt% sulfur, and 2.2 wt% PPA. While the T_g of conventional asphalt was −22°C, the T_g of the modified asphalt B-PDS was about −26 °C. This particular modified asphalt showed a dynamic material function resembling the ones for polymeric materials.

Figure 7(a)portrays the master curve of the loss tangent $\tan \delta(\bar{\omega})$ of the modified asphalt from Figure 6. In Figure 7(b), the master curve of loss tangent as the function of the temperature $\tan \delta(T)$ is portrayed. Note the low values of the loss tangent in both figures, as well as the loss tangent's deep local minimum. The origin of this deep local minimum is seen in Figure 8, where the master curve of the normalized phase angle (sample B-PDS) is depicted as a function of the temperature.
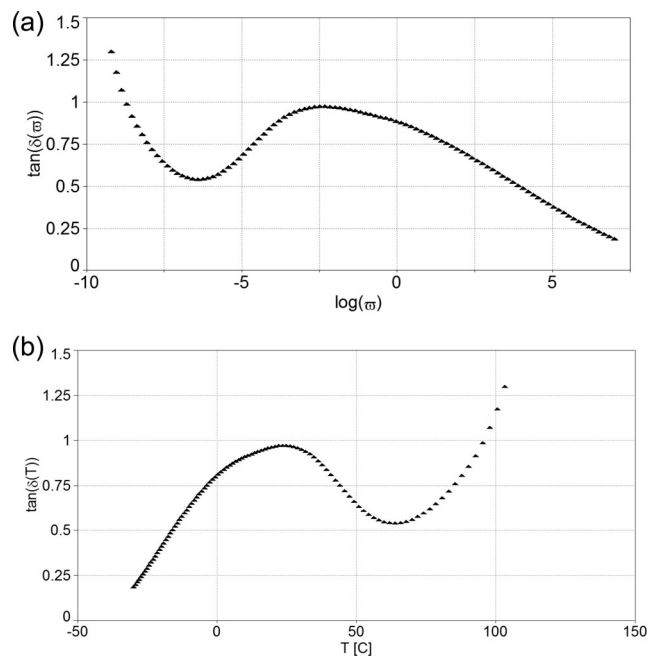

FIGURE 7 (a) Master curve of $\tan(\delta(\bar{\omega}))$ for asphalt B (200/300, penetration) + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur +2.2 wt% PPA and (b) Master curve of $\tan(\delta(T))$ for asphalt B (200/300 penetration) + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur +2.2 wt% PPA
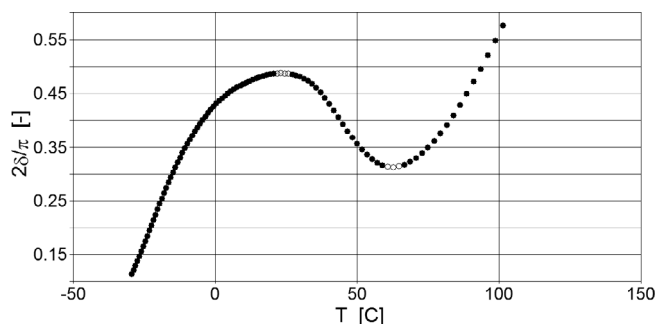

FIGURE 8 Transformation $\bar{\omega} \rightarrow T$ for asphalt B (200/300 penetration) +3 wt% SBS Kraton D1101 + 0.12 wt% sulfur+2.2 wt% PPA, ● $2\delta(T)/\pi$, ○ max/min of $2\delta(T)/\pi$

3.2 | Discussion

Two important temperatures are identified in Figure 8. The first, $T \sim 23°C$, is the temperature below which the sample B-PDS started to approach the glassy zone. The second, $T \sim 62°C$, is the temperature above which the sample started to flow and eventually approaches the terminal zone of linear viscoelasticity. Within that temperature interval (23 and 62°C) the normalized phase angle decreases as would be the case on a corresponding interval of reduced frequencies. Thus, the derivative of this
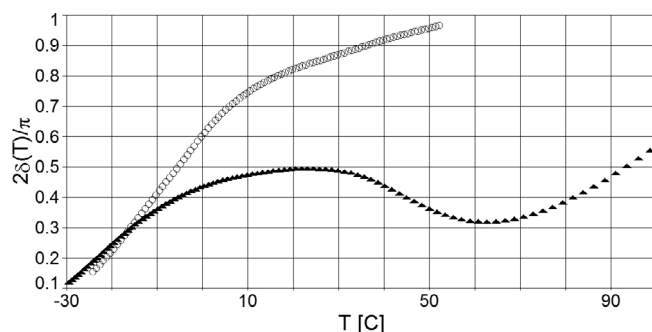
FIGURE 9 Transformation $\bar{\omega} \rightarrow T$ for $\circ$ B (200/300 penetration), ▲ B (200/300 penetration) + 3 wt% SBS Kraton D1101 + 0.12 wt% sulfur+2.2 wt% PPA

angle is negative, which leads to the appearance of the negative peak on the graph of f(MW*).

It is clear that there are two major relaxation mechanisms in the two parts of the studied modified asphalts, one for the low-apparent molecular weight and one for the high-apparent molecular weight. The question remains, what does the negative peak of f(MW*) represent? In polymers, the glassy zone is followed by the transition zone.[7] In the asphalt materials discussed in this article, the decrease of the normalized phase angle could represent the hardening phase or the phase of relatively weak cross-linking between the modified asphalt's components. Nothing like this appears in conventional asphalts.

The situation for asphalt B can be compared with the situation in the B-PDS-modified asphalt. The normalized phase angle in asphalt B decreases smoothly from higher to lower temperatures and the curve has a concave shape—no local maxima or minima were detected. The same observation for group of conventional asphalts has been made previously.[6,13]

The material function in which the linear viscoelastic behavior is summarized is the complex relaxation modulus $G*(\bar{\omega})$. By transforming the reduced angular frequency $\bar{\omega}$ to an apparent molecular weight MW*, it is possible to obtain the dynamic material functions as functions of MW*. The relationship between $\bar{\omega}$ and MW*, which serves as the calibration equation, has the form of a power law. The estimates of such relations in conventional asphalts have been used previously.[6,13,16,19]

Unfortunately, there is no unique calibration equation for conventional or modified asphalts.[9] It is only possible to estimate the two parameters of the power law calibration equation that can be used for a group of asphalt materials. Possible deviations in MWDs, obtained by the method discussed in this article, were investigated by Cuciniello et al.[9] It must be stressed that, in conventional asphalts, the normalized master phase angle is an

increasing function in any of the variables ($\bar{\omega}$ and MW*), which makes the discussed method more palatable.

In modified asphalts, it is often the case that the normalized master phase angle has a local minimum in $\bar{\omega}$ and MW*. The derivative of the normalized master phase angle with respect to log(MW*) will exhibit a negative peak. This result can be considered as lacking physical meaning unless the interpretation of the derivative (i.e., the function f(MW*)) is extended. The helping hand comes from the second transformation. With the help of the WLF form of the horizontal shifting factor,[7] $\bar{\omega}$ can be tr1ansformed to T. The glass transition temperature (or more accurately, the glass transition temperature interval) T_g is identified from the position of the maximum of G″(T). The maximum of G″(T) can be clearly identified in all the tested asphalt asphalts (conventional and modified).

In Figure 8, the normalized phase angle is plotted as a function of temperature. The transition from solid-like to liquid-like domains is seen in this interval (T ∼ 23°C, T ∼ 63°C). The decrease of the normalized master phase angle can clearly be seen on this interval. In Figure 9, this modified asphalt sample is compared with a conventional (unmodified) asphalt. The interval where the modified asphalt's normalized phase angle is decreasing is apparent. This is the interval where the negative peak of f(MW*) will appear.

Thus, in modified asphalts the short and long-time relaxation domains correspond to the relaxation of small and large mass, respectively. These two parts are divided by the interval where the material goes from solid-like to liquid-like. In the latter domain, it is difficult to assign a real mass. The same situation was observed in many different modified asphalt.[6,10,13,16]

It is well known that rheological properties of a polymer depend on its MWD.[25] One can expect the same to be true also in asphalt materials. Numerical method of obtaining the MWD via the derivatives of dynamic material functions is inherently prone to amplification of experimental noise. This problem was discussed, and the remedy was suggested in ref. 25.

4 | CONCLUSION

During the last decade of the 20th century, the Bituminous Materials Chair at University of Calgary studied the possibility of determining the MWD in asphalt binders from rheological data.[13,16] The same idea was then picked up by Themeli et al.[19] and recently also by Guciniello et al.[9] In all the previous works, various models of the complex relaxation modulus were used.

In this contribution we are analyzing the possibility to obtain the distribution of the apparent molecular

weight in conventional as well as in polymer modified asphalt binders without any rheological models chosen in advance. It was our intention to conclude a comprehensive point of view on the problem of determining the MWD in complex asphalt materials and use it for a better understanding of the internal structure of such materials.

The concept of apparent molecular weight (MW*) was used for the estimate of apparent MW*D of two different asphalt materials. The two investigated conventional asphalts differed in the value of penetration (high and low). The conventional asphalt with high value of penetration (low value of viscosity) was then modified by variety of modification technologies.

The produced modified asphalt materials MW*D exhibited one negative peak growing larger with increasing amount of modifying polymers as well as with cross-linking/curing effects of additional additives. This was expected since studied polymer modified asphalt materials had shown local minima on master curves of normalized phase angle, related to their transition from viscoelastic solids to viscoelastic liquids.

In this study was also performed the second transformation of the master curves of reduced frequency to temperature. This transformation was able to identify the virtual glass transition temperature interval in all tested modified materials, in agreement with experimentally obtained glass transitions in asphalt materials,[26] helping to understand their transition from elastic to viscoelastic solid state.

The combination of two different transformations in this method helps not only to understand the existence of negative peaks in MW*D in polymer modified asphalt materials, it provides an additional insight into their little-known internal structure.

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